

## Migration mechanism in defect metal hydrides containing superabundant vacancies

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### 1. Introduction

In the presence of interstitial H atoms, the concentration of M-atom vacancies is enhanced dramatically, forming a defect structure containing superabundant vacancies (SAVs). The diffusivity of M atoms is enhanced accordingly. Physically, these phenomena are the result of the lowering of the formation energy of a vacancy by trapping H atoms [1, 2].

A Monte Carlo calculation on the SAV formation process revealed that, in hydrides of fcc metals, two distinct defect phases are formed; a vacancy-ordered phase of high concentrations of vacancies on the  $L1_2$  structure, and a vacancy-disordered phase of relatively low concentrations where vacancies are randomly distributed over the M lattice. Transitions between these two phases take place, as shown in Fig.1 [2].

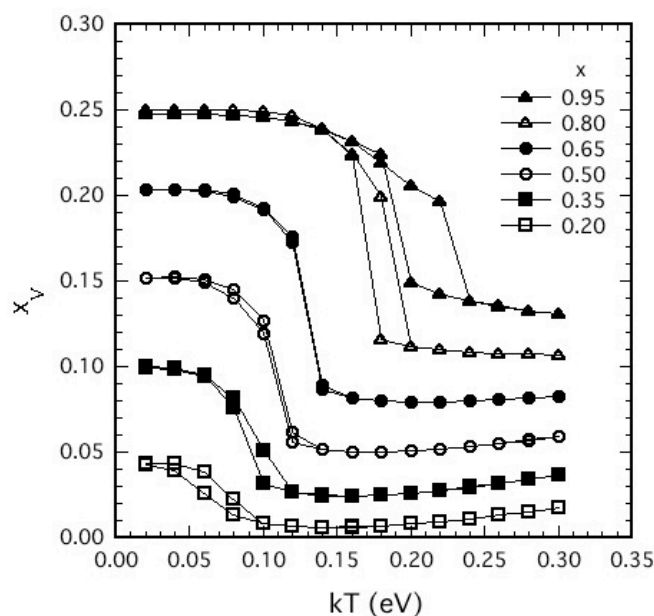


Figure 1. Temperature dependence of the vacancy concentration for several different H concentrations,  $x=[H]/[M]$ , calculated for  $e_b=0.4$  eV.

Note that, in both phases, the vacancy concentration is many orders of magnitude higher than in pure metals. The present paper addresses, specifically, the migration of H atoms and M-atom vacancies in the vacancy-disordered phase.

Experimental data available for Pd, Ni and Nb indicate that the migration energy of a vacancy is increased by amounts comparable to the migration energy of an H atom, and the pre-exponential factor is reduced by 1 ~ 2 orders of magnitude [3 ~ 5].

## 2. Calculation

The atomic jump rate varies from site to site according to variable local environments. In the present calculation, this effect is included approximately as a change in energy caused by Vac-H interaction. The energy of a vacancy with  $r$  neighboring H atoms is lowered by  $re_b$  ( $r=0, 1, 2, \dots, 6$ ), and that of an H atom with  $r'$  neighboring vacancies by  $r'e_b$  ( $r'=0, 1, 2$ ). Assuming a saddle-point energy to be everywhere the same, the jump rate of a vacancy can be written

$$W_v = W_0 \exp[-(e_m^v + re_b)/kT],$$

where  $W_v$ ,  $e_m^v$  are the jump rate and the migration energy of a vacancy, respectively. For an H atom,  $W_v$ ,  $e_m^v$  and  $r$  are to be replaced by  $W_H$ ,  $e_m^H$  and  $r'$ , respectively. The pre-exponential factor is assumed to be the same for both vacancies and H atoms.

The diffusion coefficient can be obtained by following the motion of tagged H atoms and vacancies as a function of time, *i.e.*  $D = \langle R^2 \rangle / 6t$ , where  $R$  is the atomic displacement in time  $t$ .

Actual calculations have been performed for a system consisting of  $100 \times 100 \times 100$  sites, containing H atoms of  $x=[H]/[M]=0.1$ . Energy parameters approximately corresponding to the Ni-H system have been adopted:  $e_m^v=1.0$  eV,  $e_m^H=0.4$  eV and  $e_b=0.4$  eV.

## 3. Conclusion

Results obtained for  $kT=0.15$  eV (close to the melting point) show that the diffusivity of vacancies is nearly 2 orders of magnitude smaller than that of H atoms, and reduced by another 2 orders of magnitude by trapping H atoms.

More detailed examination of the problem, including its temperature dependence, is in progress.

## References

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